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<b>(54) Title:</b> RESTORING PERMEABILITY TO A POLYMER PLUGGED WELL  <b>(57) Abstract</b>  A permeability-reducing, high molecular weight, water-soluble, synthetic, organic polymer accumulated at or near a wellbore used in an oil recovery process is degraded to a lower molecular weight by contacting the polymer with an aqueous inorganic peroxide solution to restore permeability.		

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Description

## RESTORING PERMEABILITY TO A POLYMER PLUGGED WELL

Technical Field

The invention is a process to restore diminished permeability at or near a wellbore used in an oil recovery process and, more particularly, an in situ process to chemically degrade an undesirable accumulation of a high molecular weight synthetic polymer at or near the wellbore to a lower molecular weight with an inorganic peroxide.

Background Art

Any number of high molecular weight, water-soluble polymers are commonly injected into subterranean oil-bearing formations to increase the rate or amount of oil production therefrom. The polymer is added to a chemical flood or waterflood as a viscosifier to improve the areal and vertical sweep efficiency of the flood. The polymer may also be injected in a polymer slug as a mobility buffer in sequence with a chemical slug to maintain the rheological stability of the chemical slug as it advances through a formation.

Wells used to inject the polymer for these processes often experience excessive injectivity reduction over time. Excessive injectivity reduction translates to longer injection times and a diminished rate of oil production. This problem is attributable to an accumulation of a high molecular weight polymer residual at or near the wellbore. The accumulated polymer causes permeability reduction at the injection wellbore face or in the rock matrix and fracture network near the wellbore. In a manner similar to injection wellbores, permeability reduction can occur at or near production wellbores where injected polymer is produced with the oil. On a macroscale the polymer accumulation at the wellbore face may resemble a gel-like material while on a microscale the polymer accumulation within the pores of the rock matrix may simply be the

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buildup of discrete polymer molecules. Once polymer accumulation occurs, the polymer is not readily displaced away from the wellbore by physical means and continues to build up over the duration of polymer injection or oil production.

Attempts have been made in the art to solve the problem of permeability reduction attributable to injected fluid. U.S. Patent 3,529,666 to Crowe restores permeability to a subterranean formation impaired by bacterial deposits by sequentially injecting a peroxide solution and an acid into the formation. U.S. Patent 3,556,221 to Haws et al teaches an in situ treatment of wells plugged with polymer deposits by injecting an aqueous solution having a pH greater than 8 and containing a halogenated compound such as sodium hypochlorite. U.S. Patent 4,234,433 to Rhudy et al teaches a method for treating a polymer before it is injected into a formation to reduce its plugging ability. An oxidizing chemical such as sodium hypochlorite is added to a polymer solution followed by a reducing chemical. The treated polymer solution is subsequently injected into the formation.

The literature shows that contacting an enhanced oil recovery (EOR) polymer with a sodium hypochlorite solution in a workover can have significant unintended deleterious results. See Taggart and Russell, "Stress Micellar/Polymer Flood Post Test Evaluation Well" at pp. 141-142, SPE/DOE 9781 (1981). As such, a process is needed to effectively restore wellbore permeability by degrading high molecular weight polymer accumulated at or near the wellbore in situ with minimal undesirable impacts on oil production and oil field equipment.

#### Disclosure of the Invention

The present invention provides a process to restore permeability at or near a wellbore, after the wellbore or near wellbore region has experienced excessive permeability reduction due to the accumulation of a high molecular weight polymer at its face, in the rock matrix of the near wellbore region or the fracture network in communication with the wellbore. The near wellbore region as

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defined herein is a volume up to about 3.1 radial meters from the wellbore face. Polymer accumulation is an undesirable, but sometimes unavoidable, result of injecting a high molecular weight, water-soluble, synthetic organic polymer into a subterranean formation via a well to improve oil recovery from the formation. Large accumulations of the polymer are visually detectable as a gel-like material in backflowed fluids from injection wells. Generally these gels result when the polymer accumulates in relatively large volumes, e.g., in the wellbore at the face or in the fracture network communicating with the wellbore. The mechanism for polymer gelation is not fully understood. Gelation may be caused by: polymer cross-linking induced by metal cations from numerous sources including injection water, well tubulars and the formation rock; in situ reaction of the polymer to an insoluble form; or other as yet undetermined causes. Despite the uncertainty surrounding the gelation mechanism, it is clear that these gels greatly reduce the permeability of the wellbore face and fracture network. Smaller accumulations of the polymer, which may be invisible to the eye, also excessively reduce permeability in the rock matrix near the wellbore. The accumulation of a discrete number of extremely high molecular weight polymer molecules can substantially plug small pores in the formation and greatly reduce permeability therein.

The present invention is an effective remedial in situ treatment process for attacking, degrading and dispersing the high molecular weight polymer once it has accumulated in or near the wellbore. The process comprises injecting an aqueous inorganic peroxide solution into the treatment zone, i.e., the affected wellbore, where the peroxide degrades the high molecular weight polymer on contact to a lower molecular weight. Once the polymer has been degraded, it is readily displaced from the treatment zone and permeability is restored therein. The process is broadly applicable as a remedial treatment for virtually any subterranean surface or volume occupied by a substantially immobile synthetic organic polymer, including EOR injection and production wells, strata treated with polymer gels for vertical conformance, etc.

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The present process performs significantly better than those described in the art cited above. The process is specific to the in situ degradation of a high molecular weight, water-soluble, synthetic, organic polymer. The objective can be achieved by the simple process of injecting a single aqueous inorganic peroxide slug such as hydrogen peroxide into the treatment zone.

Hydrogen peroxide is neither harmful to the operating nor external environments. It is generally compatible with the metals found in the injection equipment and wellbore casing. Hydrogen peroxide decomposes to water and oxygen. The decomposition products present almost no environmental risk.

In contrast, sodium hypochlorite poses a greater risk to the external environment because of its corrosivity. From an operational standpoint, sodium hypochlorite treatment is undesirable because it can actually reduce permeability in the treatment zone by inducing additional gel formation as shown in Taggart and Russell, supra, or by reacting with the steel injection tubing to form a wellbore plugging precipitate. The sodium hypochlorite is also very corrosive to the steel tubing used in the injection equipment and casing, thereby reducing the effective lifetime of these materials.

#### Brief Description of the Drawing

Figure 1 is a graph comparing the size distribution of a partially hydrolyzed polyacrylamide before and after hydrogen peroxide treatment as determined by high performance liquid chromatography.

#### Best Mode for Carrying Out The Invention

The process of this invention is preferably used to treat EOR polymer injection wells, exhibiting excessively diminished injectivity, i.e., excessively diminished permeability at or near the wellbore, caused by the formation and buildup of substantially immobile high molecular weight polymers at the wellbore face, in the near wellbore environment, or in the fracture network in communication with the wellbore. As noted above, the process may also be applied to EOR production wells and other subterranean regions

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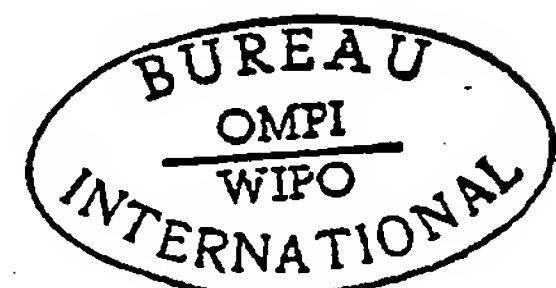
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having reduced permeability due to the accumulation of the polymer. Permeability is used broadly herein to mean either the permeability of a subterranean formation matrix or the fluid flow capacity of a wellbore. Thus, "diminished permeability at or near a wellbore" refers to both face plugging of the wellbore and permeability reduction in the formation matrix near the wellbore.

The process is initiated by injecting an aqueous solution containing an inorganic peroxide into the affected wellbore. Hydrogen peroxide is the preferred inorganic peroxide in solution at a concentration of from about 500 ppm to about 30% by weight and preferably about 1 to about 5% by weight. The preferred aqueous solvent is fresh water although in some instances formation water can be used. The pH of a hydrogen peroxide solution in fresh water is an inverse function of concentration. The normal pH of a hydrogen peroxide solution in fresh water is acidic, i.e., below 7. Within the relevant hydrogen peroxide concentration range in fresh water, the pH ranges from almost 7 at 500 ppm to about 4 at 30%. A hydrogen peroxide solution in a slightly basic formation water can have a pH value greater than 7. Generally, the hydrogen peroxide solution can be injected into the wellbore without adjusting the pH of the solution away from its normal value.

The quantity of hydrogen peroxide solution injected into the wellbore is dependent on the size of the zone to be treated. Generally a sufficient amount of solution is injected to contact all of the polymer occupying the treatment zone, which is a function of the volume of the wellbore itself, the pore volume and oil saturation of the surrounding rock, the void volume of any fracture network, the amount of polymer injected and the specific chemical characteristics of the polymer and wellbore environment.

Once the peroxide solution is injected into the wellbore it is preferable but not essential to shut in the well allowing a soak time to maximize the amount of polymer contacted and degraded by the peroxide solution. The soak time can be from several minutes up to 48 hours or more. Degradation of the polymer initiates immediately on contact with the peroxide.

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Additives, although not necessary, can be added to the peroxide solution to increase the polymer degradation rate. Useful additives in the solution include hydroxide ions and transition metal cations such as copper, iron, lead and chromium. However the beneficial effect of the hydroxide ions and metal cations in conjunction with the peroxide to degrade the polymer must be weighed against the adverse effect of the hydroxide ions and metal cations on the peroxide. They accelerate the decomposition rate of hydrogen peroxide to water and oxygen reducing the amount of peroxide available to attack the polymer. This trade-off limits the usefulness of these additives.

Polymers which may be degraded according to the process include high molecular weight, synthetic, water-soluble, organic polymers having a carbon-carbon backbone. The peroxide treatment is most effective against polyacrylamide and partially hydrolyzed polyacrylamide, wherein the molecular weight range of the polymer is from about 100,000 to about 20 million while from about 0 to about 70% of the amide groups are hydrolyzed.

Although it is not certain, laboratory data indicate that peroxide attacks the carbon-carbon bonds along the polymer backbone resulting in scission of the backbone. Backbone scission significantly reduces the molecular weight of the polymer, breaking it into smaller units, without significantly changing the chemical composition and attributes of the functional groups on the polymer. Although the degraded polymer is substantially the same species as the originally injected high molecular weight polymer, because of its lower molecular weight the degraded polymer is physically too small to accumulate and form a stable gel in the wellbore or plug the formation pores. Thus the lower molecular weight polymer has little permeability reducing effect.

After treatment of an injection wellbore, which may include more than one sequential injection of the treatment fluids, it is preferable to backflow out of the wellbore the treatment fluids, including degraded polymer, peroxide decomposition products (water and oxygen), and any residual peroxide and mobilized gel, before the

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well is placed back in service. Alternatively, the fluids resulting from the treatment can be displaced away from the near wellbore out into the formation and produced from a production well in fluid communication with the injection well. In cases where it is necessary to place an injection well back in service immediately after treatment, a water spacer is preferably injected between the treatment fluids and the subsequently injected EOR polymers to prevent diffusion mixing of the peroxide and subsequently injected polymer. Once treatment is terminated and injectivity restored to the well, injection of EOR fluids via the treated injection well may be resumed.

When the instant process is used to restore the productivity of EOR production wells plugged by high molecular weight polymers deposited at or near the production wellbore or to restore permeability to subterranean strata intentionally treated with a polymer gel such as for improving vertical conformance, the same reaction conditions as set forth above are followed.

The following examples show the effectiveness of hydrogen peroxide as a wellbore treating agent for degrading high molecular weight polymers to lower molecular weight polymers. The examples illustrate specific applications of the instant invention and are not to be construed as limiting the scope thereof.

#### EXAMPLE 1

Aqueous partially hydrolyzed polyacrylamide (PHPA) samples were placed in a series of sample jars. Either brine or fresh water solvents were added to the jars. The PHPA in each sample jar was the same, having an average molecular weight of about 4.5 million and about 30% of the amide groups hydrolyzed. An aqueous hydrogen peroxide ( $H_2O_2$ ) solution was added to each of the polymer samples except for three samples (Nos. 1, 3 and 6), which were retained as blanks. The dissolved contents of the sample jars were stirred overnight at room temperature. After 17 hours, the viscosity, screen factor and filtration factor of each test solution were measured and are recorded in Table 1 below. The column labeled

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"PHPA initial" is the weight percent concentration of PHPA in the initial sample placed in the jar. The column labeled "PHPA final" is the weight percent concentration of PHPA after the sample is diluted with H<sub>2</sub>O<sub>2</sub> solution. In samples where no H<sub>2</sub>O<sub>2</sub> is added, the values for "PHPA initial" and "PHPA final" are the same. The column labeled "H<sub>2</sub>O<sub>2</sub>" is the weight percent concentration of H<sub>2</sub>O<sub>2</sub> in the sample immediately after the H<sub>2</sub>O<sub>2</sub> is added. "Filtration factor" is defined as the time required to filter 50 cm<sup>3</sup> of polymer solution divided by the time required to filter 50 cm<sup>3</sup> of brine. Both volumes were pressure filtered through a 47 mm diameter 0.22 micron cellulose acetate Millipore filter at a pressure drop of 138 kPa.

TABLE 1

Sample No.	PHPA Initial	PHPA Final	H <sub>2</sub> O <sub>2</sub>	Aqueous Solvent	Viscosity (cp)	Screen Factor	Filtration Factor
1	0.2	0.20	0	SIW*	12	18	>720
2	0.2	0.18	2.7	SIW	2.0	1.2	1.1
3	1.5	1.5	0	fresh	6000	>250	>720
4	1.5	0.5	2.0	fresh	1.4	1.3	1.2
5	1.5	0.5	2.0	SIW	1.4	1.2	1.1
6	6.5	6.5	0	fresh	70,000	>250	>720
7	6.5	1.3	2.4	SIW	1.4	1.0	1.1

\*SIW = A synthetic oil-field injection water containing 2.6 wt.% total dissolved solids and 1.3 wt.% hardness.

Samples 1 and 2 were analyzed via size-exclusion high performance liquid chromatography (HPLC) prior to filtration. The results of HPLC are shown in Figure 1. Sample 1 has two peaks; the high molecular weight PHPA eluted first followed by all the low molecular weight material in the sample. H<sub>2</sub>O<sub>2</sub> treated Sample 2 has only one peak corresponding to low molecular weight material. The dissolved solids in Sample 4 were analyzed by infrared (IR) after filtration. The solids exhibit the same IR properties as PHPA.

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Example 1 indicates the ability of the  $H_2O_2$  to degrade all the high molecular weight PHPA to lower molecular weight PHPA as evidenced by the HPLC and IR analytical results. IR analysis tends to confirm that the mechanism for polymer degradation is backbone scission, which does not substantially change the functional groups on the polymer.

#### EXAMPLE 2

A backflowed gel was obtained from an oil field PHPA injection well. The gel contained PHPA similar to that of Example 1 in a concentration of 6500 ppm. In addition, the gel contained approximately 150 ppm of elemental iron and amounts of sand and other materials. An  $H_2O_2$  solution was added to the gel of Sample 2 while none was added to Sample 1. The two samples were stirred overnight at room temperature. The viscosity, screen factor and filtration factor were measured and are recorded in Table 2 below. Filtration factor was determined in the same manner as Example 1 except that 0.6 micron polyvinyl chloride Polyvic Millipore filters were used.

TABLE 2

<u>Sample No.</u>	<u>PHPA Gel (wt.% in sample)</u>	<u><math>H_2O_2</math> (% by wt.)</u>	<u>Viscosity (cp)</u>	<u>Screen Factor</u>	<u>Filtration Factor</u>
1	100	0	>1800	>>1000	>>1000
2	90	3	1.5	1.0	270

#### EXAMPLE 3

Solid pieces, containing about 50% by weight of cross-linked polyacrylamide, were immersed in different samples of aqueous solutions. The quantities were such that the concentration of polyacrylamide in the sample would be 10% by weight when dissolved in the solution. The sample solutions contained varying amounts of  $H_2O_2$  and were maintained at atmospheric pressure and room temperature until substantially all of the solid polyacrylamide was dissolved. Samples 1-3 were stirred well. Samples 4 and 5 were not stirred at all. Filtration factor was determined in the manner of Example 1. Samples 1-3 were filtered via a 0.22 micron mixed

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cellulose acetate and cellulose nitrate Millipore filters while Samples 4 and 5 were filtered via a 0.6 micron polyvinyl chloride Polyvic Millipore filter. The results are recorded in Table 3 below. The  $H_2O_2$  concentration is the initial concentration. It diminished with contact time.

In Sample 1, the  $H_2O_2$  concentration was restored to 3% after 22 hours. In Sample 4, the solid was broken up into 20 small pieces while in Sample 5 the solid was a single piece. In Samples 1-5, all of the solid had dissolved prior to the specified contact time (prior to 22 hours in Sample 1).

TABLE 3

<u>Sample No.</u>	<u><math>H_2O_2</math> (% by wt.)</u>	<u>Contact Time (hrs)</u>	<u>Viscosity (cp)</u>	<u>Screen Factor</u>	<u>Filtration Factor</u>
1	3.0	22	4.3	14	>50
		44	2.5	1.7	>50
2	3.0	46	3.3	1.9	>50
3	10.0	22	1.6	1.5	15
4	10.0	18	2.3	2.3	3.4
5	10.0	18	2.6	2.2	3.5

EXAMPLE 4

Two PHPA injection wells of the type in Example 2 experienced diminished injectivity as shown below in Table 4. Injectivity is expressed in liters per day at 6900 kPa injection pressure. 9500 liters of 5%  $H_2O_2$  aqueous treatment solution were injected into each well. After injection of the treatment fluids and a soak period, the treatment fluids were backflowed. The wells were then put back on water injection. The injectivity results are shown below in Table 4.

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TABLE 4

Injectivity before treatment: Well 1 = 4,600  
Well 2 = 4,700

<u>Elapsed Time After Water Injection Resumed (days)</u>	<u>Well 1 Injectivity</u>	<u>Well 2 Injectivity</u>
0.1	14,000	11,000
0.2	17,000	15,000
0.3	36,000	20,000
0.9	13,000	9,300
4	11,000	7,600
5	10,000	7,600
10	10,000	7,200

The wells appear to have stabilized after approximately 5 days. Water injection into both wells at this point is around twice the pretreatment injection rates. The first 9500 liters of the fluid backflowed immediately after treatment were clear, containing no gel and only small amounts of oil. Additional fluids backflowed after the first 9500 liters contained a small amount of gel. The appearance of small amounts of gel in the backflowed fluids indicates that only the PHPA gels directly contacted by the treatment fluid are degraded.

EXAMPLE 5

Aqueous samples, containing 1.95% by weight PHPA of Example 1, were treated with different hydrogen peroxide solutions or oxygen-containing gases. The gases were bubbled through the PHPA test solutions. The weight ratio of PHPA solution to hydrogen peroxide solution was 1:1. In the gas tests, distilled water was added to the PHPA solution in a 1:1 weight ratio. The PHPA was contacted by the treatment chemical at room temperature for 20 hours and then analyzed for viscosity, screen factor and filtration factor in the manner of Example 1. 0.6 micron Polyvic Millipore filters were used

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for the filtration factor tests at a pressure drop of 69 kPa. The results are recorded below in Table 5.

TABLE 5

<u>Treatment Solution</u>	<u>Viscosity (cp)</u>	<u>Screen Factor</u>	<u>Filtration Factor</u>
blank (no treatment chemical)	>2000	>>240	>>80
6.0% H <sub>2</sub> O <sub>2</sub>	1.6	1.4	2.9
3.0% H <sub>2</sub> O <sub>2</sub>	1.7	1.9	3.5
1.0% H <sub>2</sub> O <sub>2</sub>	3.0	1.9	4.7
Oxygen	>2000	>>240	>>80
Air	>2000	>>240	>>80

It is apparent that hydrogen peroxide is effective in degrading the PHPA while oxygen-containing gases are ineffective in degrading the PHPA.

EXAMPLE 6

A fired Berea Sandstone plug, 7.6 cm long and 2.5 cm in diameter having a permeability of 100 md, was sequentially flooded with the fluids set forth in Table 6. The fluid flood was carried out at 22°C and at a fluid pressure of 2800 kPa. Pressure taps were set over the first and second halves of the plug's length to determine the respective permeability reduction over the halves. The results are recorded below in Table 6. All flooding fluid concentrations are in weight %. The PHPA is that of Example 1. Fluid volume is the pore volumes of flooding flood fluid in each sequence. Permeability reduction is expressed as  $k_{\text{final}}/k_{\text{initial}}$ .

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TABLE 6

Sequence No.	Flooding Fluid	Fluid Volume	Permeability Reduction		Frontal Advance Rate (m/day)
			Ist Half of Plug	2nd Half of Plug	
1	1.0% NaCl	50	1.00	1.00	130
2	0.1% PHPA in 1% NaCl	50	--	--	32
3	1.0% NaCl	70	0.15	0.16	130
4	3.0% H <sub>2</sub> O <sub>2</sub>	13	--	--	21
5	1.0% NaCl	50	0.96	0.80	130

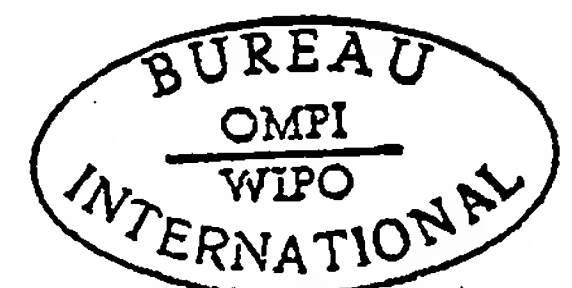
PHPA flooding in Sequence 2 resulted in an excessive permeability reduction due to the accumulation of residual PHPA in the core plug. Virtually all of the permeability was restored to the first half of the plug by H<sub>2</sub>O<sub>2</sub> treatment in Sequence 4 while 80% of the permeability was restored to the second half of the plug.

EXAMPLE 7

Three small wide-mouth sample bottles were packed with sections of metal tubing, having an outside diameter of 0.64 cm. The remaining volume of the bottles was filled with Clorox, a trademark of the Clorox Co., for a 5.25% by weight sodium hypochlorite solution, having an adjusted pH of 9. The experiments were carried out at room temperature.

The metal tubing in the first sample was carbon steel. Within minutes, large amounts of a voluminous brown precipitate formed and continued forming until more than two hours had elapsed. Monel metal tubing in the second sample produced similar results except that the precipitate was black and slightly less voluminous. Monel is a trademark for an alloy containing about 67% Ni, 28% Cu, 1-2% Mn and 1.9-2.5% Fe by weight. 316 stainless steel tubing was in the third sample. Little reaction was noted even after several days had elapsed.

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It is apparent that sodium hypochlorite readily attacks and corrodes carbon steel and Monel, which are commonly used in the oil fields, to form metal oxidation products. These precipitates are capable of effectively plugging a subterranean formation. Similar laboratory experiences with hydrogen peroxide and the above metals indicate that the peroxide is not nearly as corrosive as the sodium hypochlorite.

While the foregoing preferred embodiment of the invention has been described and shown, it is understood that all alternatives and modifications, such as those suggested and others, may be made thereto and fall within the scope of the invention.

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CLAIMS

I claim:

1. A process for restoring permeability at or near a wellbore in fluid communication with a subterranean formation, the permeability at or near the wellbore reduced by a high molecular weight, water-soluble, synthetic, organic polymer accumulated at the wellbore face, near the wellbore, or in the wellbore fracture network, the process comprising the steps of:

injecting an aqueous solution containing an inorganic peroxide into the wellbore; and

contacting the high molecular weight polymer with the inorganic peroxide until at least a portion of the high molecular weight polymer is degraded to a lower molecular weight to substantially restore the permeability at or near the wellbore.

2. The process of Claim 1 wherein the polymer is a polyacrylamide or a partially hydrolyzed polyacrylamide.

3. The process of Claim 1 wherein the inorganic peroxide is hydrogen peroxide.

4. The process of Claim 3 wherein the concentration of the hydrogen peroxide in the solution is from about 500 ppm to about 30% by weight.

5. The process of Claim 4 wherein the concentration of the hydrogen peroxide in the solution is from about 1 to about 5% by weight.

6. The process of Claim 1 wherein the aqueous solvent in said aqueous solution is fresh water.

7. The process of Claim 1 wherein transition metal cations selected from the group, consisting of lead, chromium, iron, copper, and mixtures thereof, are added to the aqueous solution.

8. The process of Claim 1 wherein hydroxide ions are added to the aqueous solution.

9. The process of Claim 1 wherein said wellbore is an oil production wellbore.

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10. A process for restoring the injectivity of an injection wellbore used to inject a high molecular weight, water-soluble, synthetic, organic polymer in an oil recovery process, the wellbore in fluid communication with a subterranean oil-bearing formation, the injectivity of the wellbore reduced by the polymer accumulated at the wellbore face, near the wellbore or in the wellbore fracture network, the process comprising the steps of:

injecting an aqueous solution containing an inorganic peroxide into the injection wellbore;

contacting the high molecular weight polymer with the inorganic peroxide until at least a portion of the high molecular weight polymer is degraded to a lower molecular weight to substantially restore the injectivity of the wellbore.

11. The process of Claim 10 wherein the polymer is a polyacrylamide or a partially hydrolyzed polyacrylamide.

12. The process of Claim 10 wherein the inorganic peroxide is hydrogen peroxide.

13. The process of Claim 12 wherein the concentration of the hydrogen peroxide in the solution is from about 500 ppm to about 30% by weight.

14. The process of Claim 13 wherein the concentration of the hydrogen peroxide in the solution is from about 1 to about 5% by weight.

15. The process of Claim 10 wherein the aqueous solvent in said aqueous solution is fresh water.

16. The process of Claim 10 wherein transition metal cations selected from the group, consisting of lead, chromium, iron, copper, and mixtures thereof, are added to the aqueous solution.

17. The process of Claim 10 wherein hydroxide ions are added to the aqueous solution.

18. The process of Claim 10 wherein the wellbore is shut-in for a soak time after the aqueous solution is injected into the wellbore and the oil recovery process is resumed after the soak time.

19. A process for restoring the permeability of a zone in a subterranean formation wherein the permeability of the zone is

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reduced by the presence therein of a high molecular weight, water-soluble, synthetic, organic polymer, the process comprising:

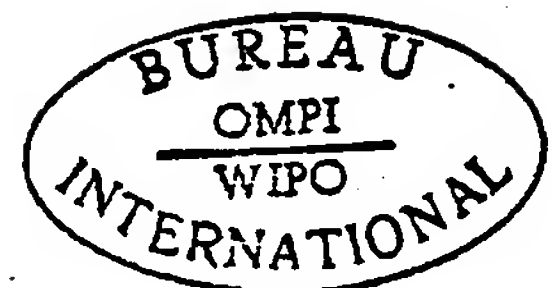
injecting an aqueous solution containing an inorganic peroxide into the zone; and

contacting the high molecular weight polymer with the inorganic peroxide until at least a portion of the high molecular weight polymer is degraded to a lower molecular weight polymer to substantially restore the relative permeability of the zone.

20. The process of Claim 19 wherein the inorganic peroxide is hydrogen peroxide.

21. The process of Claim 19 wherein the polymer is a polyacrylamide or a partially hydrolyzed polyacrylamide.

22. All inventions described herein.



## AMENDED CLAIMS

[received by the International Bureau on 25 June 1985 (25.06.85);  
original claims 1, 2, 10, 11, 19 and 21 amended; claims 23-27 new;  
other claims unchanged (3 pages)]

1. A process for restoring permeability at or near a wellbore in fluid communication with a subterranean formation, the permeability at or near the wellbore reduced by a high molecular weight, synthetic, organic polymer accumulated at the wellbore face, near the wellbore, or in the wellbore fracture network, the process comprising the steps of:

injecting an aqueous solution containing an inorganic peroxide into the wellbore; and

contacting the high molecular weight polymer with the inorganic peroxide until at least a portion of the high molecular weight polymer is degraded to a lower molecular weight polymer to substantially restore the permeability at or near the wellbore.

2. The process of Claim 1 wherein the high molecular weight polymer is a polyacrylamide or a partially hydrolyzed polyacrylamide.

3. The process of Claim 1 wherein the inorganic peroxide is hydrogen peroxide.

4. The process of Claim 3 wherein the concentration of the hydrogen peroxide in the solution is from about 500 ppm to about 30% by weight.

5. The process of Claim 4 wherein the concentration of the hydrogen peroxide in the solution is from about 1 to about 5% by weight.

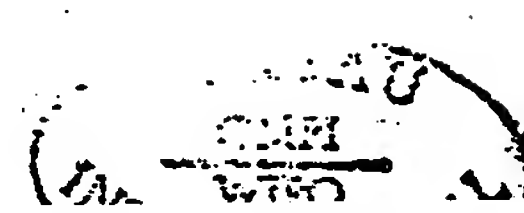
6. The process of Claim 1 wherein the aqueous solvent in said aqueous solution is fresh water.

7. The process of Claim 1 wherein transition metal cations selected from the group, consisting of lead, chromium, iron, copper, and mixtures thereof, are added to the aqueous solution.

8. The process of Claim 1 wherein hydroxide ions are added to the aqueous solution.

9. The process of Claim 1 wherein said wellbore is an oil production wellbore.

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10. A process for restoring the injectivity of an injection wellbore used to inject a high molecular weight, synthetic, organic polymer in an oil recovery process, the wellbore in fluid communication with a subterranean oil-bearing formation, the injectivity of the wellbore reduced by the polymer accumulated at the wellbore face, near the wellbore or in the wellbore fracture network, the process comprising the steps of:

injecting an aqueous solution containing an inorganic peroxide into the injection wellbore;

contacting the high molecular weight polymer with the inorganic peroxide until at least a portion of the high molecular weight polymer is degraded to a lower molecular weight polymer to substantially restore the injectivity of the wellbore.

11. The process of Claim 10 wherein the high molecular weight polymer is a polyacrylamide or a partially hydrolyzed polyacrylamide.

12. The process of Claim 10 wherein the inorganic peroxide is hydrogen peroxide.

13. The process of Claim 12 wherein the concentration of the hydrogen peroxide in the solution is from about 500 ppm to about 30% by weight.

14. The process of Claim 13 wherein the concentration of the hydrogen peroxide in the solution is from about 1 to about 5% by weight.

15. The process of Claim 10 wherein the aqueous solvent in said aqueous solution is fresh water.

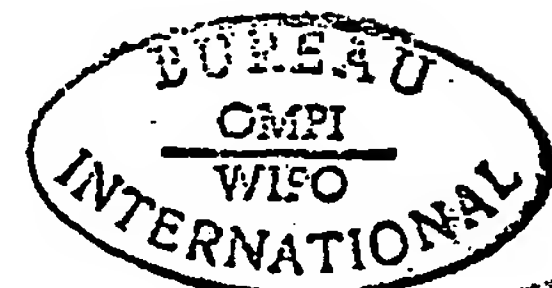
16. The process of Claim 10 wherein transition metal cations selected from the group, consisting of lead, chromium, iron, copper, and mixtures thereof, are added to the aqueous solution.

17. The process of Claim 10 wherein hydroxide ions are added to the aqueous solution.

18. The process of Claim 10 wherein the wellbore is shut-in for a soak time after the aqueous solution is injected into the wellbore and the oil recovery process is resumed after the soak time.

19. A process for restoring the permeability of a zone in a subterranean formation wherein the permeability of the zone is

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reduced by the presence therein of a high molecular weight, synthetic, organic polymer, the process comprising:

injecting an aqueous solution containing an inorganic peroxide into the zone; and

contacting the high molecular weight polymer with the inorganic peroxide until at least a portion of the high molecular weight polymer is degraded to a lower molecular weight polymer to substantially restore the relative permeability of the zone.

20. The process of Claim 19 wherein the inorganic peroxide is hydrogen peroxide.

21. The process of Claim 19 wherein the high molecular weight polymer is a polyacrylamide or a partially hydrolyzed polyacrylamide.

22. All inventions described herein.

23. The process of Claim 2 wherein the high molecular weight polymer is in the form of a gel.

24. The process of Claim 1 further comprising the step of displacing the lower molecular weight polymer away from the well-bore.

25. The process of Claim 10 wherein the high molecular weight polymer is in the form of a gel.

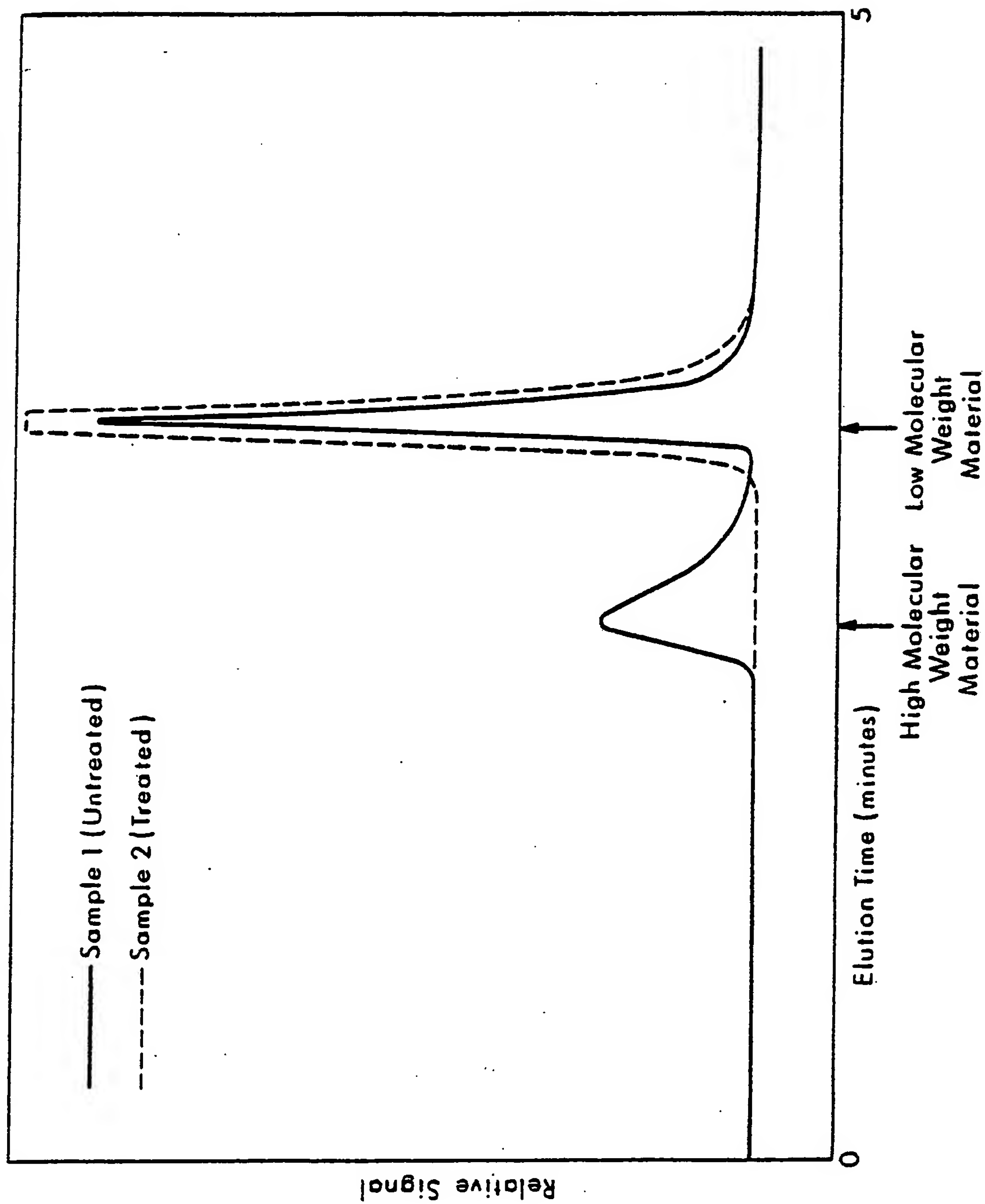
26. The process of Claim 10 further comprising the step of displacing the lower molecular weight polymer away from the well-bore.

27. The process of Claim 19 wherein the high molecular weight polymer is in the form of a gel.

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**Fig. 1**  
*HPLC Analysis of  $H_2O_2$  - Treated and Untreated PHPA Solutions*



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# INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US 84/01867**

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols are used, indicate all) <sup>1</sup> According to International Patent Classification (IPC) or to both National Classification and IPC IPC <sup>4</sup> : <b>E 21 B 43/25; E 21 B 43/22</b>																													
<b>II. FIELDS SEARCHED</b> <div style="text-align: right; font-size: small;">Minimum Documentation Searched<sup>7</sup></div> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%; border-bottom: 1px solid black; padding: 2px;">Classification System</td> <td style="border-bottom: 1px solid black; padding: 2px;">Classification Symbols</td> </tr> <tr> <td style="padding: 2px;">IPC<sup>4</sup> -</td> <td style="padding: 2px;">E 21 B</td> </tr> </table> <div style="text-align: center; font-size: x-small; margin-top: 5px;">             Documentation Searched other than Minimum Documentation              to the Extent that such Documents are Included in the Fields Searched<sup>8</sup> </div>			Classification System	Classification Symbols	IPC <sup>4</sup> -	E 21 B																							
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<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b> <table style="width: 100%; border: none;"> <tr> <th style="width: 10%; border-bottom: 1px solid black; font-size: x-small;">Category<sup>9</sup></th> <th style="width: 70%; border-bottom: 1px solid black; font-size: x-small;">Citation of Document,<sup>11</sup> with indication, where appropriate, of the relevant passages<sup>12</sup></th> <th style="width: 20%; border-bottom: 1px solid black; font-size: x-small;">Relevant to Claim No.<sup>13</sup></th> </tr> <tr> <td style="vertical-align: top; padding: 5px;">X,Y</td> <td style="padding: 5px;">US, A, 3818991 (K.H. NIMERICK) 25 June 1974 see column 19, lines 24-38; column 5, line 48 - column 6, line 5; column 8, example 8 - column 10, line 26; tables I,II,III; figures 1,2</td> <td style="vertical-align: top; padding: 5px;">1-6,9-15, 18-22</td> </tr> <tr> <td colspan="3" style="text-align: center; padding: 5px;">--</td> </tr> <tr> <td style="vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;">US, A, 4259205 (J.R. MURPHEY) 31 March 1981 see claim 1</td> <td style="vertical-align: top; padding: 5px;">7,16</td> </tr> <tr> <td colspan="3" style="text-align: center; padding: 5px;">--</td> </tr> <tr> <td style="vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;">US, A, 2483936 (P.L. ROBERTS) 4 October 1983 see column 1, lines 10-30; column 3, lines 49-51</td> <td style="vertical-align: top; padding: 5px;">8,17</td> </tr> <tr> <td colspan="3" style="text-align: center; padding: 5px;">--</td> </tr> <tr> <td style="vertical-align: top; padding: 5px;">P,X</td> <td style="padding: 5px;">US, A, 4464268 (V.H. SCHIEVELBEIN) 7 August 1984 see claims 1,2,5,6</td> <td style="vertical-align: top; padding: 5px;">1-6,8-15,17-22</td> </tr> <tr> <td colspan="3" style="text-align: center; padding: 5px;">-----</td> </tr> </table>			Category <sup>9</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	X,Y	US, A, 3818991 (K.H. NIMERICK) 25 June 1974 see column 19, lines 24-38; column 5, line 48 - column 6, line 5; column 8, example 8 - column 10, line 26; tables I,II,III; figures 1,2	1-6,9-15, 18-22	--			Y	US, A, 4259205 (J.R. MURPHEY) 31 March 1981 see claim 1	7,16	--			Y	US, A, 2483936 (P.L. ROBERTS) 4 October 1983 see column 1, lines 10-30; column 3, lines 49-51	8,17	--			P,X	US, A, 4464268 (V.H. SCHIEVELBEIN) 7 August 1984 see claims 1,2,5,6	1-6,8-15,17-22	-----		
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<div style="display: flex; justify-content: space-between; font-size: x-small;"> <div style="width: 45%;"> <p><sup>9</sup> Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"G" document member of the same patent family</p> </div> </div>																													
<b>IV. CERTIFICATION</b> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 2px;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border-bottom: 1px solid black; padding: 2px;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="padding: 2px; text-align: center;">5th March 1985</td> <td style="padding: 2px; text-align: center;">22 AVR. 1985</td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 2px;">International Searching Authority</td> <td style="border-bottom: 1px solid black; padding: 2px;">Signature of Authorized Officer</td> </tr> <tr> <td style="padding: 2px; text-align: center;">EUROPEAN PATENT OFFICE</td> <td style="padding: 2px; text-align: center;">               J. H. Rosenberg           </td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	5th March 1985	22 AVR. 1985	International Searching Authority	Signature of Authorized Officer	EUROPEAN PATENT OFFICE	 J. H. Rosenberg																			
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INTERNATIONAL APPLICATION NO.  
-----PCT/US 84/01867 (SA 8416)  
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This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 04/04/85

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3818991	25/06/74	US-A- 3779914	18/12/73
US-A- 4259205	31/03/81	GB-A, B 2005277	19/04/79
		NL-A- 7808611	10/04/79
		DE-A, C 2843452	19/04/79
		FR-A- 2416919	07/09/79
		US-A- 4199484	22/04/80
		US-A- 4216829	12/08/80
		GB-A, B 2075520	18/11/81
		US-A- 4368136	11/01/83
		SE-A- 7810508	07/04/79
US-A- 2483936		None	
US-A- 4464268	07/08/84	None	

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